

Some Physical Constants of Ammonia: a Study of the Effect of Change of Temperature and Pressure on an Easily Condensible Gas.

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This work was originally undertaken in order to obtain an accurate value for the density of ammonia, the only determination that appeared reliable being that of Le Duc.* While the experiments were in progress, the result of a determination by Guye† was published; the number differed from that of Le Duc and made a fresh determination still more desirable. We have now determined the density at temperatures ranging from -20° to $+100^{\circ}$ C., also the density at half an atmosphere pressure at 0° C. From these data the coefficient of expansion and the compressibility can be calculated. In addition to this, measurements of the pressure coefficient, of vapour-pressure, and of the density of ammonia in the presence of air, have been made.

Vapour-density of Ammonia.

Two methods were employed:—

- (1) The ammonia was pumped from the globe in which it was contained into concentrated sulphuric acid contained in U-tubes, and so weighed. The globe remained in position during each experiment.
- (2) In a few experiments the ammonia was weighed directly.

Apparatus, Method (1).—The apparatus may be divided into three parts: (a) the ammonia supply, (b) the globe and bath, (c) the absorption apparatus:

- (a) The ammonia was contained in an iron tube 20·5 cm. long and 3·5 cm. in diameter, closed by a valve B, obtained from the Scotch and Irish Oxygen Company. The outlet tube was connected by means of lead pipe (about 1 foot) and junctions of fusible alloy to the drying tubes C and D containing lime and recently fused sodium hydroxide respectively. The tube then divided into two branches, one leading to the escape tube E, about 900 mm. long, dipping under mercury, and the other to the globe G. Any

* 'Comptes Rendus,' 1897, vol. 125, p. 571.

† 'Comptes Rendus,' 1905, vol. 141, p. 51.

ammonia bubbling through the mercury was absorbed by dilute sulphuric acid contained in the wash-bottles F.

- (b) The globe of about 1.8 litres capacity was placed in (1) a thermostat containing an Ostwald toluol regulator of special pattern,* (2) in an ice bath, (3) in a bath of alcohol and solid carbon dioxide, according to the temperature required. H was an ordinary stop-cock, and K a three-way tap leading to two sets of drying bulbs L, containing strong sulphuric acid. (Only one set is shown in the diagram.)

The temperatures above 0° were measured accurately to 0.02° by means of a thermometer made by Fuess, of Berlin, and standardised at the Reichsanstalt. For temperatures below 0° a mercury thermometer was used which had been previously standardised by comparison with an air thermometer. Owing to the difficulty of maintaining the constancy of these low temperatures, we cannot claim that they were accurate to less than 0.1° .

- (c) The absorption apparatus consisted of three U-tubes, M, N, O, connected together by thick rubber tubing. M and N were stoppered. M was connected with a tube from the globe by the ground joint J, the U-tube being held in place by a rubber band. The tube O was connected with the gauge and a water air-pump not shown in the diagram. P and R were three-way stop-cocks.

Method of Work.

Filling the Globe.—Everything being in position, the globe and connecting tubes were exhausted to 0.1 mm. by means of a Töpler pump. The valve B was then opened until ammonia bubbled through the mercury in E, the taps H and K were opened, and left open until the ammonia again began to escape, when K was immediately closed.

The main part of the ammonia was then pumped out by the water air-pump through P, and the remainder by the mercury pump through R. It should be mentioned that the drying tube of the pump contained strong sulphuric acid, which immediately absorbed the ammonia thus admitted.

The globe was again filled as before. The temperature of the bath was carefully regulated, and the excess of ammonia allowed to escape into the air through P, the stop-cock R being turned on from time to time. Owing to the cooling caused by the expansion, some little time was required for the gas to acquire the exact temperature and pressure. From half an hour to an hour sufficed. In order to indicate when the pressure was equal to that of the

* 'Roy. Soc. Proc.,' 1903, vol. 72, p. 74.

atmosphere, a small mercury gauge was connected with J; it showed finally no change on turning R.

In some of the earlier experiments the water air-pump was used in the filling; in that case the globe was exhausted to $1/10$ atmosphere and filled with ammonia, the process being carried out six times.

Absorption of the Ammonia.—The connecting tubes, including H, K, were freed from ammonia and moisture by repeated exhaustion and admission of air through L. The U-tubes containing sulphuric acid and glass wool plugs soaked with it (see fig. I) were then connected up, M and N having

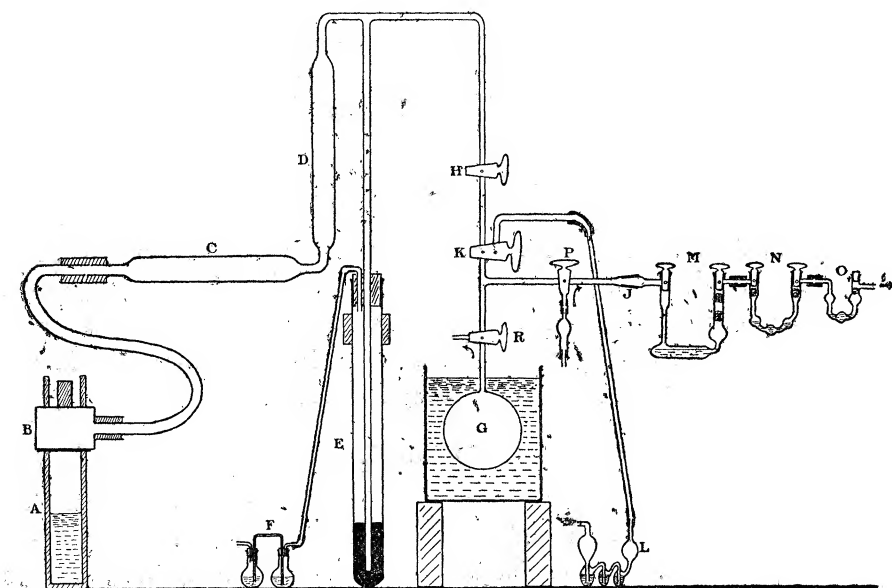


Fig. I.

been weighed. O was a guard tube to prevent the access of moisture from the pump. The connections were tested by exhausting the U-tubes and noting any change in the gauge on standing. Leaks having been shown to be absent, air was admitted through L, and the U-tubes were connected with the globe through P and R. The apparatus was then exhausted very slowly to about $1/10$ atmosphere, very nearly all the ammonia being absorbed by the sulphuric acid in M; air was admitted through L, and the apparatus again exhausted. This was done five times in all. Next, air was admitted through L, and in order to make the pressure inside the tubes exactly that of the atmosphere, connection was made through a calcium chloride tube fixed to P; M and N were closed and then removed and carefully weighed. The barometer was read immediately after the ammonia

in the globe had ceased to blow off, the readings being made accurately to 0.1 mm.

Volume of the Globe.—The globe was weighed full of dry air at known temperature and pressure, and again full of water at known temperature. From these weighings the capacity of the globe was calculated. Correction was made for the displacement of air by the weights, and the weights used in this part of the work were compared with those used in weighing the ammonia (both sets having been compared with a standard gramme).

The coefficient of expansion of the globe was found by experiments with a weight thermometer made from a broken globe. Between 18°·5 and 100°·86 the coefficient was 0.0000251.

Method (2).—The ammonia was weighed directly in a globe of about 0.5 litre capacity. The weighings were made on a short beam Oertling balance, and were carried to 0.01 milligramme. The weights were standardised with the same accuracy.

In this case the globe was attached to the rest of the apparatus by means of a ground glass joint above the stop-cock; it was exhausted by a Fleuss pump to 0.01 mm., the pressure being read on a mercury gauge by means of a cathetometer. The empty globe was weighed, then filled with ammonia and detached. The excess of ammonia was allowed to escape, and the globe was again weighed, the usual precautions being taken throughout. A similar globe was used as a counterpoise.

The volume of the globe was found by weighing it, (a) completely exhausted; (b) full of dry air at known temperature and pressure; (c) full of water at known temperature. These measurements gave two closely concordant values for the capacity of the globe.

The contraction of the globe on exhaustion was measured as follows:—The globe was nearly filled with water, leaving about 5 c.c. of air in the upper part. This air was then pumped out and the stop-cock closed. The globe was next suspended in water and weighed to 0.01 gramme. It was opened to the air and weighed again, when it was found to have lost 0.15 gramme. The weight of air admitted was negligible.

Testing for Possible Errors.

Adsorption of Ammonia by Glass.—It has been usually supposed that a considerable quantity of ammonia is “adsorbed” by glass, the adsorption progressing for some time. If so adsorbed, it might be again evolved on exhausting the globe, or it might be held permanently by the glass. An experiment was made in which the globe was filled with ammonia above the atmospheric pressure, and allowed to stand 12 hours; the excess of

ammonia was then allowed to escape, and the usual number for the density was obtained. It is thus proved that if ammonia is adsorbed it is not given off on exhausting the globe.

As a further test a globe was filled with ammonia, exhausted to 0.1 mm., and allowed to stand. The pressure was then read at intervals for some days by means of a cathetometer, but it remained constant. Further, in determining the pressure coefficient, the same conclusion was arrived at, the pressure of the ammonia in an ammonia thermometer was not found to alter after the lapse of a month.

From these experiments we are forced to the conclusion that, with carefully dried ammonia and glass, adsorption (if it takes place at all) is inappreciable.

Condensation on the Surface of the Glass.—It has been thought that ammonia will condense in the same way as water vapour on the surface of glass, and so would cause an error in density determinations in glass globes. If this were the case, different densities should be obtained if globes of different sizes were employed. We have found, however, that globes of 0.50 litre and 1.77 litres capacity respectively gave the same result. The surfaces of these are as 1:2.31, whilst the volumes are as 1:3.51. The only conclusion to be drawn is that when the ammonia and the glass are carefully dried, there is no appreciable condensation of ammonia.

Loss of Ammonia by Incomplete Absorption.—The ammonia pumped out of the globe passed into two U-tubes containing concentrated sulphuric acid (including four plugs of glass wool soaked with acid), but as in all the exhaustions, except the first, the ammonia was mixed with a large proportion of air, it was thought possible that traces of ammonia might nevertheless escape absorption. This was tested by allowing the mixture of air and ammonia at the second and the fourth exhaustions to pass through two U-tubes into an exhausted globe. The contents of the globe were then tested for ammonia by Nessler's solution, but *not a trace was found*.

Moisture from the Air.—The air made to expel the ammonia was first passed through two "potash bulbs" containing strong sulphuric acid, and the bulbs were recharged every day. On passing 5 litres of air the weight of the U-tubes remained unaltered, thus showing that none of the moisture escaped absorption.

Evaporation of Sulphuric Acid.—In order to test whether any sulphuric acid was lost by evaporation, about 8 litres of dry air were passed through the first U-tube, the sulphuric acid contained in it being heated to about the same temperature as it acquired during the absorption process. *The weight remained constant to 0.1 milligramme.*

Displacement of Air owing to Change in Volume of Sulphuric Acid caused by Absorption of Ammonia.

After the completion of an experiment, the density of the contents of the U-tube was determined, and also that of the original sulphuric acid :—

	grammes.
25 c.c. specific gravity bottle	14·29
sp. gr. bottle + H ₂ SO ₄ + NH ₃ after expt.	60·27
H ₂ SO ₄ + NH ₃ filling bottle	45·98
sp. gr. bottle + fresh H ₂ SO ₄	59·10
Fresh H ₂ SO ₄ filling bottle	44·81

If no change in volume of acid had taken place, weight of mixture filling bottle would be $44·81 + 1·38 = 46·19$ grammes (1·38 grammes = weight of NH₃ absorbed).

Change in volume produced by absorption of NH₃

$$= \frac{46·19 - 45·98}{46·19} \times 25 = 0·1 \text{ c.c. approximately.}$$

The correction for air displaced is therefore 0·00013 gramme.

Preparation of Ammonia.

Ammonia from various sources was employed :

- (1) Commercial anhydrous ammonia from an iron cylinder.
- (2) Commercial ammonia was passed through a hard-glass tube containing red-hot lime into pure hydrochloric acid; the ammonium chloride formed was heated with solution of sodium hydroxide, and the ammonia evolved was thoroughly dried by passing over quick lime and sodium hydroxide. This method was used by Guye.* In our early experiments the ammonia was condensed in a glass tube placed in a freezing mixture of ether and solid carbon dioxide; later an iron tube was used.

In order to prove the efficacy of this method of preparation in destroying pyridine, a slow stream of hydrogen was bubbled through this liquid contained in a small wash-bottle, and then passed over red-hot lime. No pyridine could be detected in the gases leaving the hard-glass tube.

A sample of ammonium chloride made by the above-mentioned method was very kindly subjected to spectroscopic examination by Dr. J. J. Dobbie, who reported that he found no indication of the presence of pyridine.

- (3) Dobbie has shown† that ammonium oxalate can be freed from pyridine by repeated recrystallisation. Some ammonium oxalate was made

* *Loc. cit.*

† 'Chem. Soc. Journ.,' 1900, Trans., vol. 77, p. 318.

from commercial oxalic acid and ammonia and recrystallised 10 times (another sample six times, which proved sufficient); the ammonia was set free by heating with potash, and condensed in a glass tube.

(4) Sodium nitrite was reduced with aluminium and sodium hydroxide solution; the ammonia was absorbed by hydrochloric acid, and again liberated by sodium hydroxide.

The main part of the ammonia used was made by method (2), and was condensed in the iron tube (see diagram) placed in ether and solid carbon dioxide. The tube was fitted up like a wash-bottle, the ammonia passing in through the long tube. To the short tube was connected a drying-tube to prevent the entrance of moisture from the air. When a sufficient quantity of ammonia had condensed, the tube was removed from the freezing mixture, placed in a vice, and the valve immediately screwed on, a leather washer being placed between the tube and the valve. The valve was then fully opened, and left for about 5 minutes in order to expel the air from the top of the tube by the rapid stream of ammonia.

After some preliminary experiments the following results were obtained:—

Method (1).

Commercial Ammonia.—Temperature 0°. Capacity of globe 1·7738 litre.

Mass of ammonia.	Barometer.	Mass of 1 litre at 760 mm.
grammes.	mm.	gramme.
1·3832	767·9	0·7718
1·3838	768·05	0·7719
1·3825	767·2	0·7721
1·3843	768·2	0·7721
Mean		0·7720
Corrected to latitude 45° and for expansion of sulphuric acid on neutralisation		0·7717

Temperature 0°. Capacity of globe 1·7738 litre.

Source of NH ₃ .	Mass of ammonia.	Barometer.	Mass of 1 litre.
	grammes.		
(2)	1·3814	767·8	0·7709
	1·3830	768·5	0·7711
(3)	1·3325	740·3	0·7712
	1·3361	742·2	0·7713
(4)	1·3696	760·8	0·7713
	1·3637	760·0	0·7711
	1·3626*	756·3	0·7713
Mean finally corrected			0·77085

* Left for 12 hours to test adsorption.

Method (2).

Capacity of globe 504·76 c.c. Temperature 0°.

Mass of ammonia.	Barometer.	Mass of 1 litre.
gramme.	mm.	
0·39206	765·7	0·77094
0·39349	768·5	0·77094
0·39306	767·7	0·77090
0·39433	770·2	0·77088
Mean		0·77091
Corrected for contraction of globe when exhausted		0·77127
Reduced to latitude 45°		0·77086

The results now available for the vapour-density of ammonia at 0° are:—

Le Duc	0·7719	} Reduced to lat. 45° and sea-level.
Guye	0·7708	
Perman and Davies (1).....	0·77085	
„ „ (2).....	0·77086	

We may venture to say that Le Duc's number is erroneous, owing to the use of unpurified ammonia. Our final result is 0·77085 (giving the greater weight to series (1)), which differs only by about one part in 15,000 from that obtained by Guye, and may be taken, we believe, as the most accurate value yet obtained for this constant.

Density of Ammonia at 50°.—Capacity of globe 1·7760 litres.

Mass of ammonia.	Barometer.	Mass of 1 litre.
grammes.	mm.	gramme.
1·1190	740·6	0·6466
1·1297	747·9	0·6464
1·1476	759·6	0·6466
1·1599	767·7	0·6466
Mean		0·64655
Mean finally corrected		0·64627

Density of Ammonia at 100°.—Capacity of globe (new) 1·7718 litres.

Mass of ammonia.	Barometer.	Mass of 1 litre.
gramme.	mm.	gramme.
0·9881	760·8	0·5571
0·9913	763·8	0·5568
0·9936	765·1	0·5570
0·9931	765·2	0·5568
Mean		0·556925
Mean finally corrected		0·55668

Density of Ammonia at -20° .—The temperature -20° was obtained by shaking solid carbon dioxide into a bath of alcohol surrounded by thick felt and thoroughly stirred. The temperature was read on a mercury thermometer and was maintained constant within $0^{\circ}\cdot 1$ by adding solid carbon dioxide in small quantities as required. The thermometer was standardised by means of an air thermometer.

Capacity of globe 903·20 c.c.

Mass of ammonia.	Barometer.	Mass of 1 litre.
gramme.	mm.	gramme.
0·7612	765·9	0·8363
0·7599	763·9	0·8370
0·7586	763·2	0·8364
0·7522	756·7	0·8364
Mean		0·8365
Mean finally corrected		0·8363

Coefficient of Expansion of Ammonia.—From the results just given the specific volumes are:—

Temperature.	Volume of 1 gramme.
-20°	1·19575 litres
0	1·2973 „
50	1·5473 „
100	1·7964 „

From these numbers the coefficients of expansion for different ranges of temperature have been calculated:—

Temperature.	Coefficient of expansion.
Between 0° and -20°	0·003914
0 + 50	0·003854
0 100	0·003847

The coefficient is seen to be much greater than that of the less easily condensible gases, and decreases with rise of temperature. Attempts were made to calculate values of a and b in van der Waals' equation from these data; it was found, however, to be impossible, the equation not representing the facts with sufficient accuracy. Taking the simple equation $pv = RT$ R is found to vary about 2 per cent. between -20° and 100° .

Temperature.	R.
-20°	0·004726
0	0·004752
50	0·004790
100	0·004816

p is here expressed in atmospheres and v in litres.

Compressibility of Ammonia.—By comparing the density at half an atmosphere with that at one atmosphere, the compressibility of ammonia may be determined. The globe was filled with ammonia in the usual way, then connected with a pressure-gauge and about half the ammonia pumped out. Next the ammonia was allowed to blow off until equilibrium had been attained, when the pressure was immediately read. The readings were made on a mirror scale, the barometer standing in the same trough being read at the same time (see fig. II). Owing to the difficulty of reading the pressure and maintaining its constancy, no great accuracy was attained; the probable error is about 0·2 mm.

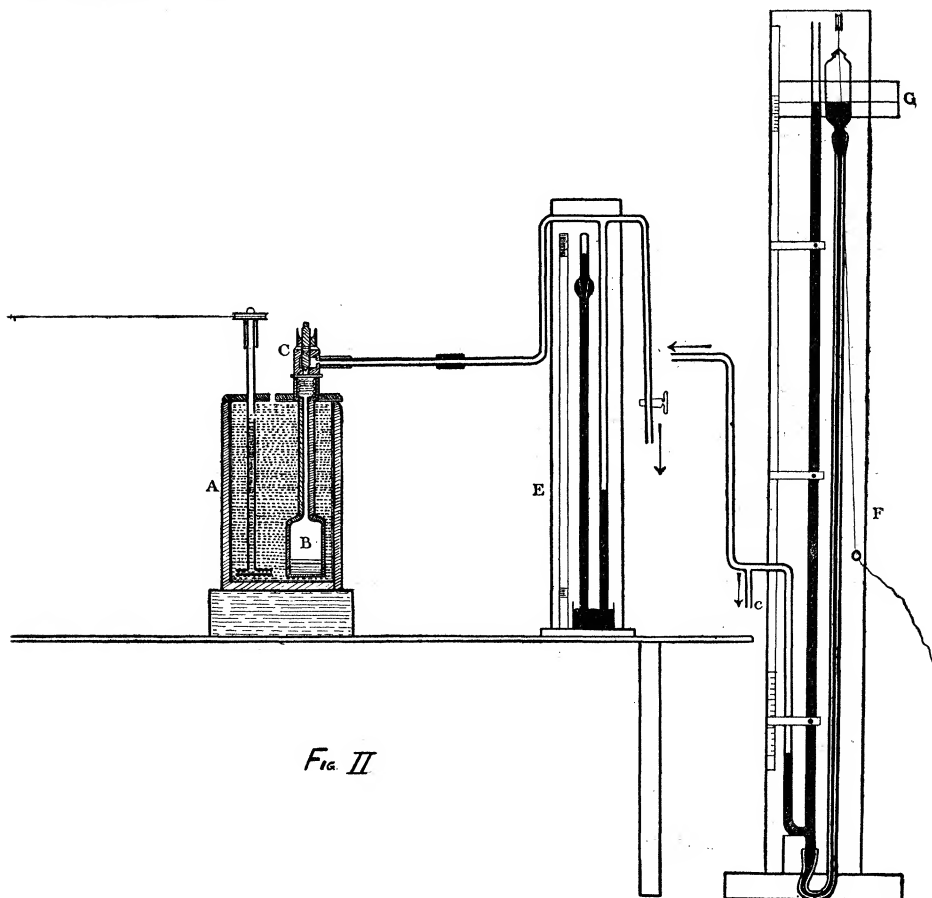


Fig. II

Density of Ammonia at Half an Atmosphere.—Capacity of globe 1·7738 litres. Temperature 0°.

Mass of ammonia.	Pressure.	Mass of 1 litre at 380 mm.
gramme.	mm.	gramme.
0·6888	385·1	0·3832
0·6859	383·1	0·3835
0·6698	374·4	0·3832
0·6811	380·6	0·3834
Mean		0·3833
Corrected for contraction of globe, expansion of acid, and latitude		0·3832

From these results

$$\frac{pv \text{ at } \frac{1}{2} \text{ atmos.}}{pv \text{ at } 1 \text{ atmos.}} = \frac{380 \times 2\cdot6096}{760 \times 1\cdot2973} = 1\cdot0058 = B.$$

As before stated, we cannot claim any great accuracy for this result, and we prefer to make use of Lord Rayleigh's number in proceeding to calculate the molecular weight of ammonia, the method and apparatus used by him being specially adapted to the purpose.* Lord Rayleigh found $B = 1\cdot00632$ at 9°·7, which, corrected in the way indicated by him, becomes 1·00706 at 0°.

This gives $\alpha = -0\cdot01413$, and the correction factor

$$\frac{1 + \alpha}{1 + \alpha_0} = 0\cdot9867.$$

Molecular weight of ammonia

$$\frac{32 \times 0\cdot77086 \times 0\cdot9867}{1\cdot4292} = 17\cdot030.$$

Taking $H = 1\cdot0076$, the atomic weight of nitrogen is deduced as 14·007, thus closely confirming the number obtained recently by several investigators.

Density of Ammonia in the Presence of Air.—Experiments were made to test the effect of admixture with air on the density of ammonia. Determinations were first made of the density of air freed from moisture and carbon dioxide by means of phosphorus pentoxide and soda-lime respectively.

Temperature 0°. Volume of globe 504·76 c.c.

Mass of air.	Pressure.	Mass of 1 litre.
gramme.	mm.	grammes.
0·65420	762·2	1·2923
0·65280	760·6	1·2923
Corrected for contraction of globe		1·2927
Reduced to latitude 45°		1·2920

* 'Zeits. für Phys. Chem.,' 1905, vol. 52, p. 705.

The globe was exhausted and weighed, about half filled with ammonia, and weighed again. It was then surrounded with ice, and air carefully admitted until the mixture had attained the atmospheric pressure. Another weighing was then made. The following are the data:—

Temperature 0°. Volume of globe 504.76 c.c.

Mass of NH ₃ .	Mass of air.	Total pressure.	Partial pressure of air.	Partial pressure of NH ₃ .	Mass of 1 litre ammonia at 380 mm.
0.18017	0.34481	755.7	401.8	353.9	0.38326
0.20274	0.31924	770.3	372.0	398.3	0.38320
		Mean corrected for latitude			0.38303

The density calculated from Rayleigh's value for the compressibility ($B = 1.00706$) is 0.38272. The partial pressure of the ammonia in the above table is obtained by subtracting the partial pressure of the air (calculated from its weight) from the total pressure. It will be seen that the density is nearly one part in 1000 higher than that calculated from the compressibility, and this represents the deviation from Dalton's law of a mixture of approximately equal volumes of ammonia and air.

The normal value of the density of ammonia, calculated from its molecular weight and the density of oxygen, is 0.7605; consequently the density of ammonia is still about 1 per cent. above the normal value, even when diluted to the extent mentioned.

Pressure-coefficient of Ammonia.—A simple form of constant volume air-thermometer, with a globe of about $\frac{1}{2}$ litre capacity, was filled with pure ammonia at about 15° C., and atmospheric pressure. In order to test if there were any inaccuracy caused by adsorption, successive readings were taken at an interval of 48 hours at 98° 1, of 24 hours at 80°, and of a month at 20°, but the readings in each case agreed within the limits of experimental error. Allowance was made for the expansion of the globe with rise of temperature. The correction for the tube connecting the globe and the gauge was inappreciable. The following are the results (see p. 40).

It will be seen at once that the numbers show a considerable deviation from van der Waals' equation, which may be written in the form $p = \frac{KT}{V} - \frac{C}{V^2}$, where K and C are constants: K is proportional to the pressure-coefficient and varies, therefore, by nearly 6 per cent. over the range of temperature employed.

The values of the pressure-coefficient are, as would be expected, very close to those obtained for sulphur dioxide, and higher than those for carbon dioxide or nitrous oxide.

Date.	Pressure corrected for temperature of mercury.	Pressure corrected for expansion of globe.	Temperature.	Pressure coefficient.
February 17	988·9 }	991·3	98°·1	0·003802
" 19	988·7 }			
" 19	939·8 }	941·7	80	0·003804
" 20	939·9 }			
" 20	886·55	887·9	60	0·003830
" 20	832·4	833·2	40	0·003850
" 20	778·0	778·4	20	0·003906
" 20	664·5	664·2	-20	0·004003
" 21	722·0	—	0	—
March 24	777·9	778·3	20	0·0039055

Summary.

(1) The vapour density of ammonia at 0° has been found to be 0·77085 (mass of 1 litre in grammes at latitude 45°), previous results being 0·7708 by Guye and 0·7719 by Le Duc.

(2) When the ammonia and the glass vessel were thoroughly dried no appreciable adsorption of ammonia by glass, or condensation of ammonia on the surface of glass, was found to take place.

(3) From density determinations at different temperatures, the coefficient of expansion of ammonia has been deduced as 0·003914 between 0° and -20°, and 0·003847 between 0° and 100°.

(4) From Rayleigh's determination of the compressibility of ammonia and our own value for the density, the molecular weight of ammonia has been calculated as 17·030, and the atomic weight of nitrogen as 14·007.

(5) Incidentally the density of air free from water vapour and carbon dioxide has been determined as 1·2920 (lat. 45°).

(6) The deviation from Dalton's law for a mixture of approximately equal volumes of air and ammonia has been found to be about 1 part in 1000.

(7) The pressure-coefficient of ammonia has been determined, the pressure being atmospheric at 15°. Between 0° and -20° the coefficient was 0·004003, and between 0° and 98° it was 0·003802.

The expenses incurred in the above research have been defrayed by a grant from the Royal Society.

APPENDIX.

Vapour Pressure of Liquid Ammonia and the Determination of its Boiling Point.

By JOHN HUGHES DAVIES.

It was suggested to me by Dr. Perman, to whom I am much indebted for kindly advice and assistance, that I should repeat the determination of the vapour pressure of liquid ammonia at some of the lower temperatures, using *pure* ammonia, in order to obtain an accurate value for its boiling point.

Apparatus.—(Fig. 2.) This consisted of:—

1. The bath A, which was a cylindrical zinc pot about 10 inches high and 6 inches diameter, covered completely on the outside with a coating of very thick felt. It contained alcohol and solid carbon dioxide, and was provided with a stirrer worked by a hot-air motor.

2. The iron tube B, which contained the liquid ammonia. This differed from the tube previously described (A, fig. 1) only in having a narrow stem.

3. The pressure gauge. Two forms of gauge were used, one for the lower temperatures, *i.e.*, temperatures at which the pressure was less than atmospheric, and the other for the higher temperatures and pressures. The former is indicated in the diagram by E and the latter by F. The pressure was read on a millimetre scale. G is a movable glass mirror of rectangular shape with a horizontal line drawn across it; by sliding it along the edge of the scale, and behind the glass tubes of the gauge, the pressure could easily be read to 1/10 mm.

4. The thermometer. A pentane thermometer was employed; it was graduated in single degrees, so that the temperature could be read accurately to 0°·1. It was standardised by means of an air thermometer.

Method of Procedure.—The apparatus being in position with the suitable pressure gauge attached and the steel valve shut off, the leading tubes were exhausted to 1/10 mm. by means of a Fleuss pump, exhaustion taking place through the stop-cock in the case of the gauge E and through the side tube C in the case of gauge F. The stop-cock was then turned off, or the side tube drawn out and fused, as the case might be. The bath was brought down to the required temperature by the addition of solid carbon dioxide; the valve C turned on, the pressure indicated by the gauge read, and the temperature of the mercury in the gauge taken.

Results.—Determinations were carried out over the range of temperature -50° to -5° .

Temperature.	Pressure (corrected).	Mean.
°		
-49·8	{ 298·0 }	297·95
	{ 297·9 }	
-41	{ 530·9 }	530·95
	{ 531·0 }	
-30	{ 867·1 }	866·95
	{ 866·8 }	
-20	{ 1393·0 }	1392·9
	{ 1392·8 }	
-15	{ 1726·3 }	1726·2
	{ 1726·1 }	
-10	{ 2146·1 }	2145·9
	{ 2145·7 }	
- 5	{ 2616·8 }	2616·9
	{ 2617·0 }	

From these results the values of the vapour pressures at equal intervals of 5° from -50° to -5° have been obtained by graphical interpolation.

Temperature.	Pressure.	Temperature.	Pressure.
°	mm.	°	mm.
-50	× 293	-25	× 1093
-45	× 421	-20	1393
-40	× 557	-15	1726
-35	× 712	-10	2146
-30	867	- 5	2617

Those pressures marked × have been obtained from the curve, whilst the others were actually observed. From this curve the boiling point of liquid ammonia at 760 mm. pressure is given as -33°·5 C.

The results obtained are found to be in very good agreement with those obtained by Regnault* and Pictet,† whilst they differ considerably from those obtained by Faraday‡ and Blümcke.§ Also the value obtained for the boiling point, viz., -33°·5, is in close agreement with the value -33°·46 obtained by H. D. Gibbs.||

* *Vide* 'Landolt und Börnstein Tabellen,' 1897 edition, pp. 77, 78.

† *Vide ibid.*

‡ 'Phil. Trans.,' 1845, p. 155.

§ 'Wied. Ann.,' vol. 34, p. 10, 1888.

|| 'Amer. Chem. Soc. Jour.,' vol. 27, p. 851, 1905.